(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number : 0 643 196 A3

(12) **EUROPEAN PATENT APPLICATION**

(21) Application number : 94304090.7

(22) Date of filing : 07.06.94

(51) Int. Cl.[6] : E21B 43/02, E21B 43/25

(30) Priority : 09.09.93 US 118702

(43) Date of publication of application : 15.03.95 Bulletin 95/11

(84) Designated Contracting States : DE DK FR GB IT NL

(88) Date of deferred publication of search report : 15.11.95 Bulletin 95/46

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(54) **Consolidatable particulate material and well treatment method.**

(57) A subterranean zone located in a well is treated by injecting a treating composition into the well to place the treating composition in the subterranean zone. the treating composition comprising a gelled carrier; a particulate material; an epoxy resin system including at least one epoxy resin; and a finely-divided hardening agent which, when dissolved, is operable for hardening the epoxy resin, the finely-divided hardening agent being dispersed in the epoxy resin system. The finely-divided hardening agent is maintained under conditions such that, prior to injecting the composition into the well, the finely-divided hardening agent does not substantially dissolve.

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European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 94 30 4090

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
A	US-A-4 972 906 (S. J. MC DANIEL) SEE COLUMN 8, LINES 49-56 ---		E21B43/02 E21B43/25
A	EP-A-0 493 786 (TOHO RAYON CO., LTD.) ---		
A	US-A-4 483 888 (YULIN WU) ---		
A	EP-A-0 313 243 (HALLIBURTON CO.) ---		
A,D	US-A-5 128 390 (J. R. MURPHEY ET AL.) -----		
			TECHNICAL FIELDS SEARCHED (Int.Cl.6)
			E21B C08G

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	21 September 1995	Devisme, F

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
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E : earlier patent document, but published on, or after the filing date
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EPO FORM 1503 03.82 (P04C01)

(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number: 0 643 196 A2

(12) EUROPEAN PATENT APPLICATION

(21) Application number: 94304090.7

(51) Int. Cl.[6]: E21B 43/02, E21B 43/25

(22) Date of filing: 07.06.94

(30) Priority: 09.09.93 US 118702

(43) Date of publication of application:
15.03.95 Bulletin 95/11

(84) Designated Contracting States:
DE DK FR GB IT NL

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The present invention relates to a method of treating a subterranean formation using a consolidatable epoxy resin-coated particulate material.

Consolidatable epoxy resin-coated particulate materials have been used heretofore in various well treatment operations. Consolidatable epoxy resin-coated sands have been used, for example, for gravel packing, for the development of controlled permeability synthetic formations within subterranean zones, and as proppant materials in formation fracturing operations. Due to their desirable permeability and compressive strength characteristics, consolidatable epoxy resin-coated particulate materials are especially well-suited for treating semiconsolidated and unconsolidated formations which contain loose or unstable sands.

As used herein, the term "consolidatable epoxy resin-coated particulate material" refers to a particulate material which is coated with an uncured or only partially cured epoxy resin composition. Typically, the consolidatable epoxy resin-coated particulate material will be injected into a subterranean zone using procedures whereby the epoxy resin does not substantially harden until after the particulate material has been delivered to a desired location within the formation. The consolidatable epoxy resin-coated particulate material will typically harden within the formation to form a hard, consolidated, permeable mass.

Well treatment methods utilizing consolidatable epoxy resin-coated particulate materials are disclosed, for example, in U.S. Patent No. 5,128,390. The entire disclosure of U.S. Patent No. 5,128,390 is incorporated herein by reference.

U.S. Patent No. 5,128,390 discloses a method for continuously forming and transporting consolidatable resincoated particulate materials. In the method of U.S. Patent No. 5,128,390, a stream of gelled aqueous carrier liquid is continuously mixed with a particulate material (e.g., sand), a hardenable epoxy resin composition, and a surface active agent. The resulting continuous composition is delivered to and/or injected into a desired subterranean zone. As the continuous mixture flows down the well tubing toward the subterranean zone, the composition ingredients are thoroughly mixed such that the gel-suspended particulate material is coated with the hardenable epoxy resin composition. After being placed in the subterranean zone, the epoxy resin composition is allowed to harden whereby the resin-coated particulate material forms a hard, permeable, consolidated mass.

The hardenable epoxy resin composition used in the method of U.S. Patent No. 5,128,390 is generally composed of: a polyepoxide resin carried in a solvent system; a hardening agent; a coupling agent; and a hardening rate controller. The hardening agent used in the method of U.S. Patent No. 5,128,390 is either (a) an amine, a polyamine, an amide, and/or a polyamide dissolved in a suitable solvent or (b) a liquid eutectic mixture of amines diluted with methyl alcohol.

Unfortunately, well treatment methods of the type disclosed in U.S. Patent No. 5,128,390 are not well-suited for use in high temperature subterranean formations. Consolidated epoxy/hardener compositions of the type used in the methods of U.S. Patent No. 5,128,390 typically cannot withstand temperatures substantially exceeding about 200° F. However, such temperature conditions are commonly encountered in subterranean formations.

Thus, a need presently exists for a consolidatable resincoated particulate material and method which can be used for treating high temperature subterranean zones and formations (i.e., zones and formations having temperatures exceeding about 200° F).

Diaminodiphenylsulfone (DDS) has been used heretofore as a hardener in certain epoxy resin compositions. DDS generally provides high temperature resistance and high chemical resistance properties. At ambient conditions, DDS is typically a solid material which will not substantially dissolve in most of the solvents and/or diluents used in epoxy resin systems. Thus, when blending DDS with an epoxy resin, the blend components must typically be heated sufficiently to enable the DDS to be dissolved in the epoxy resin system.

In view of the difficulties encountered when blending DDS with epoxy resins, the use of DDS as an epoxy resin hardener in well treatment operations has not heretofore been a viable alternative. The heating and blending operations required for dissolving DDS in epoxy resin systems typically cannot be economically and conveniently conducted at the well site. Additionally, it is generally not possible to perform the blending operation off-site and then deliver the DDS/epoxy resin blend to the well site since: (a) the resulting DDS/epoxy resin composition will typically have a very short pot life; (b) the DDS/epoxy resin composition will, in many cases, harden before it can be delivered to the well site and used; and (c) even if the blend does not harden before use, any excess material produced and delivered to the well site is simply wasted.

We have now devised a method of treating a subterranean formation using an epoxy resin-coated particulate material composition.

According to the present invention, there is provided a method of treating a subterranean zone in a well, which method comprises the steps of:

(a) injecting a treating composition into the well to place the composition in the said, subterranean zone; wherein the treating composition comprises a gelled carrier, a particulate material, an epoxy resin system

including at least one epoxy resin, and a finely-divided hardening agent which, when dissolved, is operable for hardening said epoxy resin, at least a portion of said finely-divided hardening agent being dispersed in said epoxy resin system; and

(b) maintaining the finely-divided hardening agent under conditions such that, prior to injecting the composition into the well in accordance with step (a), the finely-divided hardening agent is not substantially dissolved.

One preferred finely-divided hardening agent for use in the invention is 4,4'-diaminodiphenylsulfone.

The present invention resolves various problems encountered heretofore in the use of DDS and similar high temperature hardening agents. The components of the well treating composition can be conveniently and economically blended at the well site using standard mixing techniques and devices. Since the finely-divided hardening agent used in the inventive composition does not substantially dissolve until after the composition is pumped into the well, there is very little chance that the epoxy resin component of the composition will significantly harden before the composition is properly placed downhole. Once in place, the composition consolidates to form a hard permeable mass having a significantly higher compressive strength and a substantially higher fracture conductivity than does uncoated sand. Thus, the composition and method are well-suited for use in gravel packing operations, fracturing procedures, and other such well treating techniques.

If desired, the epoxy resin and finely-divided hardening agent components of the inventive composition can be premixed to provide a one package epoxy system having a desirably long pot life. The inventive one package epoxy system will not substantially harden until the temperature of the system is raised sufficiently to cause a significant amount of the finely-divided hardening agent to dissolve. When, for example, the finely-divided hardening agent used in the inventive one package system is 4,4'-diaminodiphenylsulfone, the one package system can typically be stored for more than 25 days at temperatures not substantially exceeding 75° F.

Further objects, features, and advantages of the present invention will be readily apparent to those skilled in the art upon reading the following description of the preferred embodiments.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

As indicated above, the inventive well treating composition comprises: an epoxy resin system; one or more finely-divided hardening agents which, when dissolved, is (are) operable for hardening the epoxy resin system; a gelled carrier; and a particulate material. The inventive well treating composition can optionally include one or more members selected from the group consisting of: a solvent or solvent system for the epoxy resin system; a diluent or diluent system for the hardening agent; one or more coupling agents; one or more compounds which are operable for crosslinking the epoxy resin system; various surfactants; hardening rate controllers; methanol; and one or more aliphatic alcohols.

The epoxy resin system used in the inventive well treating composition is composed of one or more epoxy resins which (a) will coat the particulate material when the particulate material is suspended in the gelled carrier and (b) will harden when placed downhole such that the epoxy resin-coated particulate material is thereby consolidated to form a hard permeable mass. Examples of epoxy resins preferred for use in the present invention include: the diglycidyl ethers of bisphenol-A; the diglycidyl ethers of bisphenol-F; the glycidyl ethers of aminophenols; the glycidyl ethers of methylenedianiline; and epoxy novolac resins. The epoxy resins used in the inventive well treating composition will preferably have epoxide equivalent weights (EEW) in the range of from about 90 to about 300. The EEW of an epoxy resin is determined by dividing the molecular weight of the epoxy resin by the number of epoxide groups contained in each molecule of the epoxy resin.

The epoxy resin system used in the inventive well treating composition can also include a solvent or solvent system. When used, the solvent or solvent system will preferably be included in the epoxy resin system in an amount sufficient to ensure that the viscosity of the epoxy resin system does not substantially exceed about 5000 centipoise at 75° C. Examples of solvents suitable for use in the epoxy resin system include polar organic diluents which are reactive with epoxide and polyepoxide resins; polar organic diluents which are substantially nonreactive with epoxy resins; and mixtures thereof. Examples of suitable reactive polar organic diluents include: butylglycidylether; cresolglycidylether; alkylglycidylether; phenylglycidylether; and generally any other glycidyl ether which is miscible with the epoxy resin(s) used. Examples of substantially nonreactive polar organic diluents suitable for use in the epoxy resin system are disclosed in U.S. Patent No. 5,128,390. Preferred nonreactive polar organic diluents include: ethylacetate; butyl lactate; ethyl lactate; amyl acetate; ethylene glycol diacetate; and propylene glycol diacetate.

When possible, any solvent used in the inventive well treating composition will preferably be a material in which the finely-divided hardening agent will not substantially dissolve at ambient conditions.

The epoxy resin system is present in the inventive well treating composition in an effective amount for con-

solidating the particulate material to form a hard permeable mass. Typically, the amount of epoxy resin system used in the inventive composition will be an amount providing in the range of from about 1 to about 20 pounds of epoxy resin per 100 pounds of particulate material. When, for example, the epoxy resin system consists essentially of a mixture of N,N,N',N'-tetraglycidyl-4,4'-methylenebisbenzamine and 1,4-butanediol diglycidyl ether, the amount of epoxy resin system used in the inventive composition will preferably be an amount providing in the range of from about 2 to about 5 pounds of epoxy resin per 100 pounds of particulate material.

The hardening agent used in the inventive well treating composition can generally be any hardening agent which: (a) can be provided in finely-divided form; (b) can be readily dispersed in the epoxy resin system; (c) can be maintained under conditions such that it will not substantially dissolve prior to being injected into a well; and (d) will operate, when dissolved, to harden the epoxy resin system. The hardening agent is preferably a material which will provide a hardened epoxy resin composition which (a) exhibits substantially higher compressive strength and fracture conductivity properties than does uncoated sand and (b) substantially retains these properties at temperatures of at least about 325° F. Most preferably, the hardening agent is an agent which will yield a hardened epoxy resin composition which is well-suited for use at temperatures in the range of from about 200° F to about 350° F.

Examples of finely-divided hardening agents preferred for use in the present invention include: 4,4'-diaminodiphenylsulfone, 3,3'-diaminodiphenylsulfone, metaphenylenediamine, 4,4'-[1,4-phenylene(1-methylethylidene)]bis(benzenamine), and 4,4'-[1,4-phenylene(1-methylethylidene)]bis(2,6-dimethylbenzenamine). Due to their relative low solubilities in most epoxy resin systems, aromatic diamines are particularly well-suited for use in the present invention.

The hardening agent most preferred for use in the inventive well treating composition is 4,4'-diaminodiphenylsulfone (4,4'-DDS). The solubility of 4,4'-DDS in most epoxy resin systems is typically very low. Additionally, hardened epoxy resin compositions provided through the use of 4,4'-DDS are highly temperature-resistant and chemical-resistant. Further, hardened epoxy resin compositions formed through the use of 4,4'-DDS are particularly well-suited for temperatures in the range of from about 200° to about 350° F. Moreover, in comparison to other hardening agents used in the art, 4,4'-DDS presents an extremely low health risk.

The amount of finely-divided hardening agent used in the inventive well treating composition is an amount which, when dissolved, is effective for hardening the epoxy resin system. If the hardening agent used in the inventive composition is finely-divided 4,4'-DDS, said 4,4'-DDS is preferably included in the inventive composition in an amount in the range of from about 25 g to about 45 g per 100 g of epoxy resin.

The individual particles of the finely-divided hardening agent will preferably have sizes in the range of from about 1 to about 100 microns. Such particulate materials can be prepared, for example, by grinding the hardening agent in a mill.

In order to facilitate component blending, the finely-divided hardening agent can be added to the well treating composition in a slurry form. Examples of diluent liquids preferred for use in forming the hardening agent slurry include methanol, ethanol, isopropyl alcohol, ethyl acetate, butyl lactate, toluene, xylene, isoamyl alcohol, isohexyl alcohol, and mixtures thereof. When possible, the diluent will preferably be a liquid material in which the finely-divided hardening agent will not substantially dissolve at ambient conditions.

Although the gelled carrier liquid used in the inventive well treating composition can generally be any gelled carrier commonly used in the art, the gelled carrier liquid is preferably a gelled aqueous composition. The gelled aqueous composition can generally be formed using fresh water, brine, seawater or the like.

Generally any gelling agent commonly used in well treating operations to form gelled aqueous carrier liquids can be used in the present invention. The gelling agents preferred for use in the present invention are polysaccharides having molecular weights in the range of from about 100,000 to about 4,000,000. Polysaccharides having molecular weights in the range of from about 600,000 to about 2,400,000 are particularly well-suited for use in the present invention. The polysaccharide gelling agent will preferably include hydroxyethyl or other substituents which provide water hydration and other characteristics conducive to the formation of a clear aqueous gel having a viscosity of at least about 30 centipoise on a Fann V.G. meter at 300 rpm. Examples of polysaccharide polymers preferred for use in the inventive well treating composition include: substituted carboxy and hydroxy alkyl cellulose (e.g., hydroxyethyl cellulose and carboxymethyl hydroxyethyl cellulose); guar gum; and guar gum derivatives (e.g., hydroxy propyl guar). The gelling agent used in the inventive composition is most preferably either hydroxypropyl guar or carboxyethyl hydroxypropyl guar and most preferably has a propylene oxide substitution of from about 0.1 to about 0.7 moles of propylene oxide per mole of mannose and galactose contained in the guar.

The amount of polysaccharide gelling agent used in forming the gelled, aqueous carrier liquid will preferably be an amount in the range of from about 20 to about 120 pounds of gelling agent per 1000 gallons of water. The gelled aqueous carrier liquid will preferably have a viscosity in the range of from about 10 centipoise to about 400 centipoise. Most preferably, the gelled aqueous carrier liquid is comprised of from about 30 to about

50 pounds of hydroxypropyl guar gelling agent per 1000 gallons of water and has a viscosity in the range of from 15 to about 100 centipoise.

The gelled aqueous carrier liquid can also include one or more gel crosslinking agents. Examples of gel crosslinking agents preferred for use in the present invention include: titanium lactate; titanium triethanolamine; aluminum acetate; magnesium oxide; and zirconium salts.

The inventive well treating composition preferably also includes one or more gel breakers. The gel breakers preferred for use in the inventive composition are materials which are operable for breaking the aqueous carrier gel, and thereby reducing the viscosity of the aqueous carrier liquid, at a time substantially corresponding to the placement of the inventive composition in a desired subterranean zone. When the carrier liquid gel is broken, the carrier liquid readily separates from the remainder (i.e., the epoxy resin-coated particulate portion) of the well treating composition. As a result, the epoxy resin-coated particulate material is allowed to consolidate and thereby form a hard permeable mass in the subterranean zone.

When the gelling agent used in the inventive composition is a substituted cellulose-type gelling agent, the gel breaker used will preferably be an enzyme-type gel breaker (e.g., cellulase) or an oxidant such as sodium persulfate. When the gelling agent used in the inventive composition is a substituted guar gelling agent, the gel breaker will preferably be a hemicellulase or an oxidant such as sodium persulfate.

The particulate material used in the inventive composition can generally be any proppant or other water-insoluble particulate material of the type used in fracturing, gravel packing, and similar well treating operations. Examples include: sand; glass beads; nut shells; metallic pellets; gravel; synthetic resin pellets; gilsonite; coke; sintered alumina; mullite; and combinations thereof. The particulate material used in the present invention is most preferably sand. The particulate material will preferably have a particle size distribution in the range of from about 10 to about 70 mesh, U.S. sieve series.

The amount of particulate material used in the inventive composition is preferably an amount in the range of from about 2 to about 20 pounds of particulate material per gallon of the gelled aqueous carrier liquid. Most preferably, the amount of particulate material used in the inventive composition is an amount in the range of from about 3 to about 15 pounds of particulate material per gallon of gelled carrier liquid.

One or more coupling agents can optionally be used in the inventive composition to facilitate the coupling of the epoxy resin(s) with the particulate component of the inventive composition. Coupling agents preferred for use in the inventive composition are functional silanes. The coupling agent used in the inventive composition is preferably a N-beta-(aminoethyl)-gamma-aminopropyltrimethoxysilane. The amount of coupling agent used in the inventive composition will preferably be in an amount in the range of from about 0 to about 2 parts by weight per 100 parts by weight of epoxy resin used in the inventive composition.

As will be understood by those skilled in the art, hardening rate controllers (i.e., retarders or accelerators) can be used to extend or shorten the time necessary for curing the epoxy resin composition. Examples of retarders suitable for use in the present invention include low molecular weight organic acid esters (e.g., alkyl esters of low molecular weight alkyl acids containing from about 2 to about 3 carbon atoms). Examples of accelerators suitable for use in the inventive composition include: 2,4,6-tris dimethylaminomethylphenol; the ethylhexanoate salt of 2,4,6-tris dimethylaminomethylphenol; and weak organic acids such as fumaric acid, erythorbic acid, ascorbic acid, and maleic acid. Any hardening rate controller used in the present invention will preferably be present in an amount in the range of from about 0 to about 10 parts by weight per 100 parts by weight of epoxy resin used in the composition.

The inventive well treating composition can further include one or more surfactants which enable the epoxy resin system to rapidly coat the particulate material. Examples of such surfactants suitable for use in the present invention and desirable concentrations thereof are disclosed in U.S. Patent No. 5,128,390.

In order to further facilitate the coating of the particulate material, the inventive composition can also include an aliphatic alcohol which is only slightly water-soluble. Examples of preferred aliphatic alcohols include isoamyl alcohol and isohexyl alcohol. When used, such alcohols are preferably present in the inventive composition in an amount in the range of from about 1 to about 2.5 gallons per 1000 gallons of gelled aqueous carrier liquid.

As will be understood by those skilled in the art and as explained in U.S. Patent No. 5,128,390, the inventive composition can also include other surfactants which operate as oil-water demulsifiers, foaming agents, and the like.

The inventive well treating composition can be conveniently formed at the well site. In forming the inventive composition, the gelled aqueous carrier liquid is preferably first prepared by combining the gelling agent with water. The resulting gelled aqueous carrier is then preferably conducted to a continuous stream mixing tub or other commonly used continuous mixing apparatus. In the mixing tub, the remaining components of the inventive composition are continuously added to and mixed with the gelled aqueous carrier liquid. As the components are mixed, the resulting mixture is continuously drawn from the mixing tub and injected into the well

such that the inventive composition is placed or injected into a desired subterranean zone.

As the inventive composition flows down the well tubing toward the subterranean zone, the inventive composition is thoroughly blended such that: (a) the particulate material is suspended in the gelled aqueous carrier liquid; (b) the components of the epoxy resin system are thoroughly blended; (c) the finely-divided hardening agent is thoroughly blended with the epoxy resin system; and (d) the particulate material is thoroughly coated with the epoxy resin system/finely-divided hardening agent blend.

In one embodiment of the inventive method, the inventive well treating composition is injected into a well under sufficient pressure to form fractures in a subterranean formation. The resin-coated particulate material deposits and consolidates in these fractures to provide fluid-permeable flow paths within the formation.

In another embodiment of the inventive method, the inventive well treating composition is used in an otherwise conventional gravel packing operation. In the inventive gravel packing operation, the inventive well treating composition is delivered, for example, to an open subterranean zone (e.g., an underreamed well bore) surrounding a screening device (e.g., a perforated liner wrapped with a wire screen) whereby the resin-coated particulate material deposits and consolidates around the screening device to form a hard, fluid-permeable mass.

If desired, the epoxy resin system and finely-divided hardening agent components of the inventive composition can be premixed to form an inventive one-package epoxy system. Thus, a large batch of the inventive one-package epoxy system can be prepared and stored at a desired location. Portions of the one-package system can then be delivered, when needed, to one or more well sites.

In order to prevent the inventive one-package system from hardening, the system is maintained under temperature conditions such that the finely-divided hardening agent does not substantially dissolve in the epoxy resin system. Consequently, the finely-divided hardening agent used in the present invention will preferably be a hardening agent which will not substantially dissolve in the epoxy resin system at temperatures of up to at least about 25° C.

In one embodiment of the present invention, the inventive one-package epoxy system is prepared a substantial period (e.g., at least one day) in advance of the time that the inventive well treating composition containing the one-package system is to be injected into a well. When the hardening agent used in the inventive one-package system is 4,4'-DDS, the one-package system can generally be stored at temperatures not exceeding about 75° F for a period of more than 25 days. Substantial dissolution of the 4,4'-DDS hardening agent typically will not occur until the temperature of the epoxy resin system is raised to about 90° F.

Throughout the inventive well treatment method, the finely-divided hardening agent is preferably maintained under temperature conditions such that the hardening agent does not substantially dissolve in the epoxy resin system until after the inventive well treating composition is injected into the well. When the inventive composition is exposed to the elevated temperatures existing in the subterranean zone, the finely-divided hardening agent dissolves in the epoxy resin system and then operates to harden the epoxy resin whereby the resin-coated particulate material forms a hard, consolidated, permeable mass.

The following examples are presented in order to further illustrate the present invention.

EXAMPLE I

The viscosity development characteristics of an epoxy resin system at 100° F and 120° F were evaluated over several days. The epoxy resin system consisted of 66 grams of MY0500 (a diglycidyl ether of para-aminophenol available from CIBA GEIGY Corporation) mixed with 7.92 grams of 1,4-butanediol diglycidyl ether. The results of these tests are provided in Table 1. The results indicate that the epoxy resin system will undergo self-polymerization at elevated temperatures without the addition of a hardening agent. Such self-polymerization is likely to occur as a result of the presence of tertiary nitrogens in the backbone of the epoxy resin molecule.

In view of these results, it is apparent that the epoxy resin used in the inventive composition will preferably be a resin which will not substantially self polymerize at ambient conditions prior to the time at which the inventive composition is properly placed in the desired subterranean zone.

TABLE 1

VISCOSITY* (cps) OF EXAMPLE I EPOXY RESIN SYSTEM

	Viscosity at (°F)	
Days	100°F	120°F
0	80000	72000
1	76000	72000
2	76000	72000
3	80000	76000
5	92000	80000
6	80000	80000
7	80000	80000
8	76000	80000
9	76000	80000
10	80000	80000
11	92000	88000
12	88000	
15	80000	
20	80000	
25	88000	
30	92000	
36	108000	

* Measured with RVT Brookfield viscometer at 1 rpm with spindle #4.

EXAMPLE II

55.44 g of 4,4'-DDS powder in 4 ml of butyl lactate were mixed with 98.6 g of an epoxy resin system identical to the epoxy resin system tested in Example I. The resulting dispersion was divided in four portions. Portions 1, 2, 3, and 4 were maintained, respectively, at room temperature (i.e., about 75° F), at 90° F, at 100° F, and at 120° F. The viscosity of each composition was monitored over a number of days.

As indicated in Table 2, the dispersion maintained at room temperature did not substantially harden during the entire 26 day testing period. The compositions maintained at 90° F and 100° F, on the other hand, underwent significant hardening after four days and two days, respectively.

Thus, the one-package epoxy system tested in this Example would appear to have a relatively long pot life when stored at temperatures not substantially exceeding 75° F.

TABLE 2

VISCOSITY OF THE ONE-PACKAGE EPOXY SYSTEM PREPARED IN EXAMPLE II

Days	Viscosity* at (°F) RT**	90°F	100°F	120°F
0	36000	48000	16000	32000
1	36000	36000	24000	40000
2	36000	28000	16000	64000
3	36000	36000	24000	160000
4	44000	32000	24000	640000
5	44000	44000	28000	1600000
6	48000	44000	32000	
7	48000	72000	36000	
8	48000	88000	80000	
9	20000	112000	80000	
10	20000	240000	160000	
11	20000	256000	232000	
12	20000	400000	432000	
13	20000	688000	944000	
14	20000	1472000	1600000	
15	16000	1600000		
26	16000			

* Measured with RVT Brookfield viscometer at 1 rpm with spindle #4.

** Room temperature (i.e., about 75° F).

EXAMPLE III

Numerous one-package epoxy systems were prepared by mixing powdered 4,4'-DDS with various epoxy resin systems. The compositions of these one-package systems are set forth in Table 3. In some cases, the powdered 4,4'-DDS composition used in the blending process was a powdered 4,4'-DDS/methanol slurry.

Each of the one-package epoxy systems was used to coat a sand material suspended in a carrier. In each instance, the resin mixture in question was added to an amount of the sand/carrier suspension and the resulting composition was blended for 3 minutes using an overhead stirrer. The sand/carrier used in each case contained 8 pounds of sand per 100 gallons of carrier liquid.

Following the coating procedure, each of the resin-coated particulate materials was cured. Table 4 provides the curing conditions used in each case as well as the type of sand used, the amount of one-package system used per sack of sand, and the carrier liquid used in each case.

Following the curing process, the compressive strengths, glass transition temperatures, and melt temperatures of the resulting consolidated materials were determined. These properties are provided in Table 4.

As indicated in Table 4, the one-package epoxy/DDS dispersions provided by the present invention were effective for coating suspended sand and for providing consolidated materials having compressive strengths substantially exceeding the compressive strength of uncoated sand.

The glass transition temperature (Tg) of a cured epoxy resin generally indicates the upper useful temperature limit of the cured resin. As indicated in Table 4, almost all of the hardened compositions prepared in this Example had glass transition temperatures exceeding 200° F. Several of the hardened compositions exhibited glass transition temperatures approaching or exceeding 350° F.

TABLE 1 EPOXY SYSTEM COMPOSITIONS USED FOR SAND COATING

Components[1]	Compositions 1	2	3	4	5	6	7	8	9	10	11	12	13	14
MY0500[2]	0.83	0.83	0.83	0.83	0.83	0.83	0.83	0.83	0.83	0.83	0.83	0.83	0.83	0.83
MY720[3]														
RD-2[4]	0.17	0.17	0.17	0.17	0.17	0.17	0.17	0.17	0.17	0.17	0.17	0.17	0.17	0.17
ER-1[5]														
HY 976[6]	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Methanol (mL/g of HY 976)							0.1	0.25				0.1	0.1	0.1

TABLE 1 (Continued)

	Compositions													
Components[1]	15	16	17	18	19	20	21	22	23	24	25	26	27	28
MY0500[2]	0.83	0.83	0.83	0.83	0.83	0.83	0.83	0.83	0.83	0.83	0.83	0.33		
MY720[3]													0.80	0.80
RD-2[4]	0.17	0.17	0.17	0.17	0.17	0.17	0.17	0.17	0.17	0.17	0.17		0.20	0.20
ER-1[5]												66		
HT 976[6]	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Methanol (mL/g of HT 976)	0.1	0.1	0.1	0.1	0.1	0.1					0.1			

(1) Unless otherwise indicated, all component concentrations are expressed in terms of gram equivalents. For an epoxy resin, the weight amount of the epoxy resin corresponding to one equivalent equals the molecular weight of the epoxy resin divided by the number of epoxide groups contained in the epoxy resin molecule. For 4,4'-diaminodiphenyl sulfone an equivalent corresponds to 62 g.

(2) Diglycidyl ether of para-aminophenol available from CIBA-GEIGY Corporation.

(3) N,N,N',N'-tetraglycidyl-4,4'-methylenebisbenzenamine available from CIBA-GEIGY Corporation.

(4) 1,4-butanediol diglycidyl ether available from CIBA-GEIGY Corporation.

(5) EPI-REZ® 5071 available from Rhone-Poulenc. EPI-REZ® 5071 consists of a blend of 89% by weight of a diglycidyl ether of bisphenol A and 11% butyl glycidyl ether.

(6) Powdered 4,4'-diaminodiphenyl sulfone available from CIBA-GEIGY Corporation.

TABLE 4

SAND COATING RESULTS

Composition	Cure Time (Hours)	Cure Temp (°F)	Sand Type	Gallons of Composition Used Per Sack of Sand	Carrier Liquid	RT[4]	250°F	275°F	Tg[5] (°F)	Tm[6] (°F)
1	20	250	Resieved[7]	1/2	Water	5021	3954		257	302
2	20	250	Resieved	1/2	A[1]	2318	1622		266	345
3	20	250	Resieved	1/2	A	845	655		212	279
4	72	300	Resieved	1/2	A	3521	2357		325	396
5	72	300	Resieved	1/2	Water	4684	4095		325	396
6	20	275	Resieved	3/8	A	728		507	320	356
7	20	275	Resieved	3/8	A	2618		1528	311	347
8	20	275	Resieved	3/8	A	516		379	320	356
9	65	275	Resieved	3/8	A	2137		1998	347	376

Composition	Cure Time (Hours)	Cure Temp (°F)	Sand Type	Gallons of Composition Used Per Sack of Sand	Carrier Liquid	RT[4]	250°F	275°F	Tg[5] (°F)	Tm[6] (°F)
10	65	275	Frac	3/8	A	377		715	347	376
11	65	275	Resieved	3/8	A	2878		1803	356	380
12	20	275	Resieved	3/8	A	1732		1260	338	365
13	20	275	Resieved	3/8	A	2488		1092	320	349
14	20	275	Frac	3/8	A	852		497	302	342
15	44	275	Frac	3/8	A	2137		456	302	342
16	44	275	Resieved	3/8	A	1766		600	347	367
17	20	275	Resieved	3/8	A	1010		650	311	342
18	20	275	Frac	1/2	B[2]	1392		743	302	338
19	20	275	Frac	1/2	C[3]	1305		1373	284	347
20	20	275	Frac	1/2	B	2185		1486	284	347
21	20	275	Frac	1/2	B	1902		1121	302	351

1.5 mL of N-beta-(aminoethyl)-gamma-aminopropyltrimethoxy-silane,41.58 grams of HT976, and 11.55 mL of methanol was prepared by mixing using an overhead stirrer. A first portion of this composition was used to coat 20/40 mesh Ottawa frac sand at a concentration of 0.5 gallons of the one-package epoxy system per 100 lb. sack of sand. A second portion of the one-package system was used to coat 20/40 mesh Ottawa frac sand at a concentration of 0.375 gallons of the one-package system per 100 lb. sack of sand. The procedure used in each case for coating the sand with the one-package system involved the steps of: suspending the sand in a gelled aqueous carrier liquid at a concentration of 8 pounds of sand per 100 gallons of gelled liquid; adding the one-package epoxy system to the sand/carrier liquid suspension; and blending the resulting composition for 3 minutes using an overhead mixer. The gelled carrier liquid had a pH of 9.5 and was composed of 40 lb. of hydroxypropyl guar per 1000 gallons of aqueous liquid. The aqueous liquid used was an aqueous 2% KCl solution.

Each of the resin-coated sand compositions was cured for 24 hours at 275° F and 1000 psi closure pressure in an API linear conductivity cell.

Following the curing procedure, water flow was initiated through each of the conductivity cells and the conductivities of the materials therein were determined. Flow conductivities for each of the materials were then determined at closure pressures of 4000 psi and 6000 psi. The conductivity values obtained in these tests are recorded in Table 5.

For comparison purposes, the fluid conductivity of uncoated 20/40 Ottawa sand was also determined at closure pressures of 1000 psi, 4000 psi, and 6000 psi. The results of these tests are also shown in Table 5.

As indicated in Table 5, the fluid conductivities of the consolidated materials prepared using the inventive one-package epoxy system substantially exceeded the fluid conductivities of the uncoated sand.

At the end of the flow conductivity test, each of the consolidated compositions remained consolidated. Scanning electron microscope analysis indicated that the hardened epoxy surface coatings formed in each case were not in any way substantially disrupted by the high pressure flow tests.

TABLE 5

FRACTURE CONDUCTIVITY DATA

Stress (psi)	Conductivity (md-ft)		
	.375 gal/sack	.5 gal/sack	No Resin
1000	5385	5614	4231
4000	4225	3040	2422
6000	3029	2416	950

EXAMPLE V

A dispersion consisting of 41.58 grams of HT 976 powder, 66 grams of MYO500, 7.92 grams of RD-2, and 3 milliliters of butyl lactate was prepared by mixing with an overhead stirrer. 1.5 milliliters of N-beta-(aminoethyl)-gamma-aminopropyltrimethoxy silane coupling agent and 11.55 milliliters of methanol were added to the dispersion and mixed therewith using said overhead stirrer.

A portion of the resulting mixture was used to coat 20/40 mesh Ottawa frac sand in an amount of 0.5 gallons of mixture per 100 lb. sack of sand. A second portion of the mixture was used to coat 20/40 mesh Ottawa frac sand in an amount of 0.75 gallons of mixture per 100 lb. sack of sand. During the sand coating process, the sand was suspended in an aqueous gel having a pH of 9.5 and consisting of 40 pounds of hydroxypropyl guar per 1000 gallons of aqueous 2% KCl solution. In each case, the sand/gelled carrier suspension consisted of 8 pounds of sand per 100 gallons of the gelled aqueous carrier liquid. The sand coating procedure used was essentially identical to the coating procedure described in Example III.

Each of the resin-coated sand compositions was cured in an API linear conductivity cell for 20 hours at a temperature of 275° F. After hardening, each of the consolidated materials had a compressive strength of 1300 psi at 275° F. At a closure pressure of 600 psi, the 0.5 gallon per sack material exhibited a flow conductivity of 2500 md-ft whereas the 0.75 gallon per sack material exhibited a flow conductivity of 3000 md-ft. Since, as indicated above, the fracture conductivity of uncoated 20/40 mesh Ottawa frac sand under these conditions is only 950 md-ft, the hardened inventive compositions exhibited fracture conductivities substantially exceed-

ing the fracture conductivity of uncoated sand.

EXAMPLE VI

Twelve epoxy novolac based one-package epoxy systems (i.e., resin system compositions 29-40) having the compositions set forth in Table 6 were prepared. Resin system compositions 29-33 were prepared by mixing together 19 g of SU 2.5, 3.3 g of HELOXY 5044, 1 mL of ED-1, and 7.56 g of HT 976 for 150 minutes using a mechanical stirrer. To this mixture was added 0.5 mL of A1120 followed by 15 minutes of additional stirring. Next 3 mL of methanol were added followed by 5 additional minutes of stirring. The resulting mixture was then used, in the amounts set forth in Table 6, to coat 20/40 mesh Ottawa sand in an aqueous gel carrier.

Resin system compositions 34-36 were prepared by mixing together 19 g of SU 2.5, 3.3 g of HELOXY 5044, 1 mL of ED-1, and 0.5 mL of A1120 for 15 minutes. Next 7.56 g of HT 976 dispersed in 7 mL of methanol were added followed by one minute of additional stirring. The resulting mixture was then used in the amounts set forth in Table 6 to coat 20/40 mesh Ottawa sand in an aqueous carrier gel.

Resin system compositions 37-40 were prepared by mixing together, in the amounts set forth in Table 6, SU 2.5, HELOXY 5044, and A1120 for 15 minutes using a mechanical stirrer. A second composition containing HT 976, ED-1, and methanol in the amounts set forth in Table 6 was prepared by mixing these components together for 10 minutes using a mechanical stirrer. The second composition was added to the first composition and the resulting mixture was stirred for one minute. The final stirred mixture was then used in the amounts set forth in Table 6 to coat 20/40 mesh Ottawa sand in an aqueous carrier gel.

The gelled aqueous carrier liquid used in each case contained 40 lb. of hydroxypropyl guar per 1000 gallons of aqueous liquid (i.e., 2% aqueous KCl solution) and had a pH of 5. In each case, the sand/carrier liquid suspension used consisted of 500 g of sand per 555 mL of gelled aqueous carrier liquid.

In each case, the sand was coated with the resin composition by mixing the resin composition with the sand/carrier suspension using an overhead stirrer. Following the coating procedure, each of the resin coated sand materials was packed in a separate glass tube and cured in an oven. The curing conditions used, as well as the compressive strengths and glass transition temperatures exhibited by the cured materials, are recorded in Table 6.

As indicated by the compressive strength and glass transition temperature characteristics exhibited by compositions 29-40, these epoxy novolac based resin systems provided consolidated materials which were well-suited for use at temperatures exceeding 300° F.

TABLE 6

COMPOSITIONS TESTED IN EXAMPLE VI

RESIN SYSTEM COMPONENTS[1]	29	30	31	32	33	34	35	36	37	38	39	40
SU 2.5[1]	0.83	0.83	0.83	0.83	0.83	0.83	0.83	0.83	0.83	0.83	0.83	0.83
HELOXY 5044[1]	0.17	0.17	0.17	0.17	0.17	0.17	0.17	0.17	0.17	0.17	0.17	0.17
HT 976[2]	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
ED-1[4] (mL/g of HT 976)	0.13	0.13	0.13	0.13	0.13	0.13	0.13	0.13	0.32	0.32	0.32	0.32
Methanol (mL/g of HT 976)	0.40	0.40	0.40	0.40	0.40	0.93	0.93	0.93	0.32	0.32	0.32	0.48
A1120[5] (mL/g of HT 976)	0.022	0.022	0.022	0.022	0.022	0.022	0.022	0.022	0.022	0.022	0.022	0.022

CONSOLIDATED BLEND

	29	30	31	32	33	34	35	36	37	38	39	40
Gallons of Resin System Used per Sack of Sand	3/8	3/8	3/8	3/8	3/8	1/2	3/8	1/2	3/8	1/2	3/8	3/8

Curing Temp. (°F)	275	275	275	275	275	275	275	275	275	275	275	275
Curing Time (Hours)	20	70	20	44	20	20	20	20	20	20	20	20
Compressive Strength at 72° F (psi)	3042	---	3494	3252	2165	2553	3538	1378	2556	3260	2052	1353
Compressive Strength at 275° F (psi)	1148	---	1370	1058	365	1339	1050	935	1064	1169	1357	270
Tg (°F)	248	338	311	333	302	311	311	275	302	320	288	279
Tm (°F)	311	351	334	352	347	336	336	347	342	347	329	339

(1) Multifunctional epoxy novolac resin available from Rhone-Poulenc.

(2) Trimethylolethane triglycidyl ether available from Pacific Anchor.

(3) 4,4'-diaminodiphenylsulfone available from CIBA-GEIGY.

(4 Butyl lactate.

(5) N-beta-(aminoethyl)-gamma-aminopropyl-trimethoxysilane available from Union Carbide.

(6) Unless otherwise indicated, all component concentrations are expressed in terms of gram equivalents. For an epoxy resin, the weight amount of the epoxy resin corresponding to one equivalent equals the molecular weight of the epoxy resin divided by the number of epoxide groups contained in the epoxy resin molecule. For 4,4'-diaminodiphenyl sulfone an equivalent corresponds to 62 g.

Claims

1. A method of treating a subterranean zone in a well, which method comprises the steps of:
   (a) injecting a treating composition into the well to place the composition in the said, subterranean zone; wherein the treating composition comprises a gelled carrier, a particulate material, an epoxy resin system including at least one epoxy resin, and a finely-divided hardening agent which, when dissolved, is operable for hardening said epoxy resin, at least a portion of said finely-divided hardening agent being dispersed in said epoxy resin system; and
   (b) maintaining the finely-divided hardening agent under conditions such that, prior to injecting the composition into the well in accordance with step (a), the finely-divided hardening agent is not substantially dissolved.

2. A method according to claim 1, further comprising the step, prior to step (a), of premixing the finely-divided hardening agent with the epoxy resin system.

3. A method according to claim 2, wherein the finely-divided hardening agent is premixed with the epoxy resin system at least one day prior to step (a).

4. A method according to claim 2 or 3, wherein said finely-divided hardening agent is premixed with said epoxy resin system by mixing with said epoxy resin system a slurry comprising the finely-divided hardening agent and a carrier liquid.

5. A method according to claim 4, wherein the carrier liquid is methanol, ethanol, isopropyl alcohol, ethyl acetate, butyl lactate, toluene, xylene, isoamyl alcohol, isohexyl alcohol, or any mixture of two or more thereof.

6. A method according to any of claims 1 to 5, wherein the epoxy resin system further includes at least one solvent.

7. A method according to any of claims 1 to 6, wherein the treating composition is prepared by:
   (i) adding the particulate material to a substantially continuous stream comprising water and a gelling agent; and
   (ii) adding the epoxy resin system and the finely-divided hardening agent to said continuous stream.

8. A method according to any of claims 1 to 7, wherein the finely-divided hardening agent is 4,4'-diaminodiphenylsulfone.

9. A method according to any of claims 1 to 8, wherein said subterranean zone is a subterranean formation and said treating composition is injected into the well under sufficient pressure to fracture the subterranean formation.

10. A method according to any of claims 1 to 9, wherein the treating composition is injected into the well such that the particulate material is coated with the epoxy resin system and the finely-divided hardening agent, and the coated particulate material is deposited in said subterranean zone around a screening device.

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